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Pyrochlore to perovskite phase transformation in sol-gel derived lead-zirconate-titanate thin films

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Pyrochlore to perovskite phase transformation in sol-gel derived lead-zirconate-titanate (PZT) films was studied by x-ray diffraction and transmission-electron microscopy (TEM). X-ray diffraction studies of PZT films on sapphire substrates indicated that the pyrochlore to perovskite phase transformation was completed at 650 °C. In contrast, TEM investigations of free-standing PZT films showed that the phase transformation was completed at much higher temperatures. This discrepancy in the behavior of free-standing films versus films on substrate can be related to the size effect.

There is considerable interest in ferroelectric thin films, particularly in the lead-zirconate-titanate (PZT) system for their potential applications in high-density dynamic random-access memory (DRAM) capacitors and nonvolatile memories. Sol-gel process, sputtering, and electron-beam evaporation[1–3] are some of the thin-film processing techniques used to produce the PZT films. In general, as-deposited films are amorphous and post-deposition annealing is needed to transform the film from the amorphous structure to the desirable ferroelectric-perovskite phase. The amorphous structure will first transform into an intermediate pyrochlore phase[4] and then the pyrochlore phase will transform into the perovskite phase at a higher temperature.

Although the presence of this intermediate pyrochlore phase is commonly observed,[1] few efforts have been made to study the pyrochlore to perovskite transformation of the PZT thin films. This letter reports our findings on the microstructural changes throughout the transformation by transmission-electron microscopy (TEM). A simple and unconventional technique for the TEM sample preparation was used in this study.

In this study, the PZT films were fabricated from a metallo-organic solution (0.25 M) of lead acetate, zirconium *n*-propoxide, and titanium isopropoxide dissolved in acetic acid and *n*-propanol. This solution was then hydrolyzed to form the precursor. Details of this precursor preparation are similar to that suggested by Yi, Wu, and Sayer.[5] This precursor was then spin casted onto the single-crystal sapphire substrates and the TEM grids. The films were air dried for 5 min and then annealed at different annealing temperatures for 15 min in air.

Conventional TEM sample preparation for ceramic materials usually requires mechanical polishing, dimpling, and ion milling. This process is tedious, time consuming, and prone to introduce defects and artifacts. A novel TEM sample-preparation method, which is particularly suitable for the sol-gel process, was used in this experiment. In this study, the sol was spin coated at 3000 rpm for 30 s directly onto 400 mesh platinized-nickel TEM grids. The surface tension held the liquid film in place and the film was air dried and then annealed in the furnace. The final film thickness is estimated to be around 700 Å. This method is expeditious and does not need any mechanical polishing or ion-beam bombardment. In general, it is difficult to prepare good ceramic TEM samples by the conventional method, but almost all of the TEM samples in this study prepared by the spin-cast method are successful. Using the new preparation method, the film is fabricated without the support of a substrate. The behavior of this free-standing film may be quite different from that of the film deposited on a substrate and this difference has to be taken into consideration when the results are interpreted.

The presence of pyrochlore is commonly recognized when the amorphous PZT films are annealed to form the perovskite phase;[1] however, there is little consensus about exact peak positions and (*hkl*) identification of the pyrochlore structure because a standard diffraction file[7] of the PZT pyrochlore phase has not been established. Okada[2] observed few pyrochlore peaks located at *d* spacings of 2.95, 2.60, and 1.84 Å using Cu $K\alpha$ x-ray radiation. In this study, a computer program developed by Weidemann,[6] was used to calculate the theoretical peak positions and the intensities of the PZT perovskite and pyrochlore phases. The comparison of the peak positions and peak intensities of the perovskite phase and the pyrochlore phase from the theoretical calculation and from the standard diffraction file[7] is tabulated in Table I. The comparison of the PZT perovskite phase shows excellent agreement between the experimental results and the computed results. In this study, the x-ray diffraction of the pyrochlore phase shows only two very broad peaks at *d* spacings of 3.02 and 2.62 Å. The comparison of the computed results of the pyrochlore phase and the results obtained in this experiment by x-ray diffraction and TEM electron diffraction also show very good agreement. The advantage of the electron diffraction over the x-ray diffraction is that many more peaks can be located such that positive identification of the pyrochlore phase is possible.

In this study, x-ray diffraction was used to study the phase transition as a function of the annealing temperature. The PZT films were deposited on single-crystal sapphire disks and annealings were performed in a quartz-tube furnace at predetermined temperatures for 15 min in air. The final film thickness is about 1700 Å. X-ray diffraction results show that when the as-deposited film was annealed

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TABLE I. X-ray diffraction data of perovskite and pyrochlore phases.

		Perovskite[b]		
hkl	d^b	$d_{calc}{}^c$	$I/I_0{}^a$	$I/I_{0\ calc}{}^c$
001	4.15	4.15	9	8
100	4.04	4.04	12	16
101	2.89		100	100
110	2.85			
111	2.35	2.35	15	8
002	2.07	2.97	9	7
200	2.02	2.02	16	12
102	1.84	1.84	5	4
201	1.81	1.81	}6	4
210	1.81	1.80		4
112	1.68	1.68	12	14
211	1.66	1.66	25	26
022	1.44	1.44	9	8

		Pyrochlore[d]		
hkl	$d_{calc}{}^c$	$I/I_{0\ calc}{}^c$	d_{xray}	d_{tem}
111	6.04	31	···	···
311	3.16	14	···	···
222	3.02	100	3.02	3.03
400	2.62	31	2.62	2.63
331	2.40	10	···	···
511	2.02	6	···	···
440	1.85	52	···	1.85
531	1.77	8	···	···
622	1.58	44	···	1.58
444	1.51	9	···	···
800	1.31	8	···	1.31
662	1.20	18	···	1.20

[a]Any peak with $I/I_0 < 5\%$ is not tabulated.
[b]JCPDS card No. 33-784.
[c]Calculated from the "powder" computer program.
[d]Zr/Ti = 53/47. x ray: observed by x-ray diffraction in this study. tem: observed by TEM electron diffraction in this study.

at 450 °C, no definitive peak was observed and the film remained amorphous. As annealing temperature increased to 550 °C, two very broad pyrochlore peaks were found at 2θ of 29.5° and 34°. At 600 °C, both perovskite and pyrochlore phases were presented. Formation of a single-perovskite phase was observed at or above 650 °C.

From the x-ray diffraction of the PZT sample annealed at 550 °C, the pyrochlore phase is the only phase present and has a very broad (222) peak. The average diameter of the crystal size can be related to the peak broadening[8] and calculated to be around 6 nm. Figure 1 is a bright-field/dark-field pair of micrographs showing a homogeneous, fine-grain phase where the dark field was taken from a small area of the most intense ring. The crystal size as measured from the dark-field micrograph is around 8 nm, which agrees very well with the result from the x-ray diffraction. The diffraction-ring pattern is indexed according to the *d* spacings for the pyrochlore phase listed in Table I. Hence, we can identify this fine-grain structure as pure-pyrochlore phase. Figure 2 shows two particles that are found on a homogeneous-pyrochlore background. The particle in Fig. 2(a) can be identified as the perovskite phase by the spot pattern. The *d* spacings measured from the spot pattern match very well with the *d* spacings listed in Table I. The pyrochlore-perovskite transformation involved a

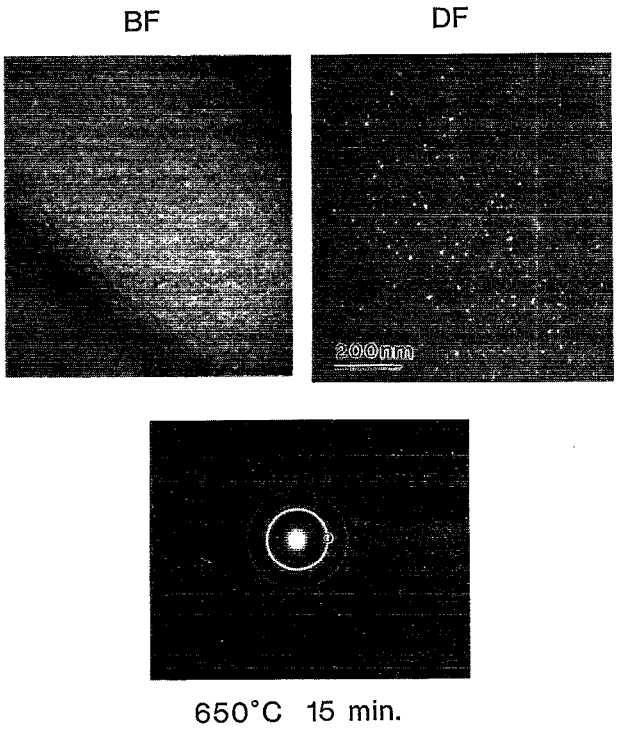

FIG. 1.(a) Bright field, (b) dark field, and (c) selected area diffraction of the pyrochlore phase showing very fine-grain structure.

volume change (5.7 vol %) and this volume change will induce strain in the perovskite phase. For a very thin, free-standing film, as in this case, the strain can be partially relieved by bending the thin perovskite particles, and all the perovskite particles found at temperatures from 650 to 700 °C had bend contours. At higher annealing temperatures, all the pyrochlore phase transformed to the perov-

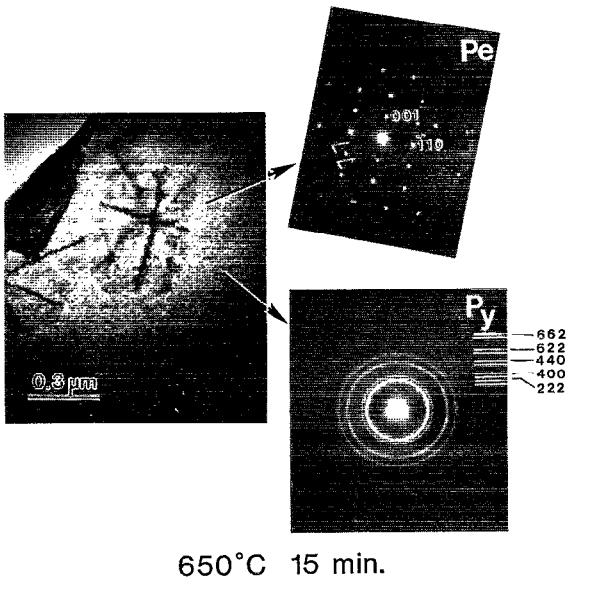

FIG. 2. TEM micrographs of the perovskite particles growing on the pyrochlore phase: (a) bright field image, (b) perovskite diffraction pattern, and (c) pyrochlore diffraction pattern.

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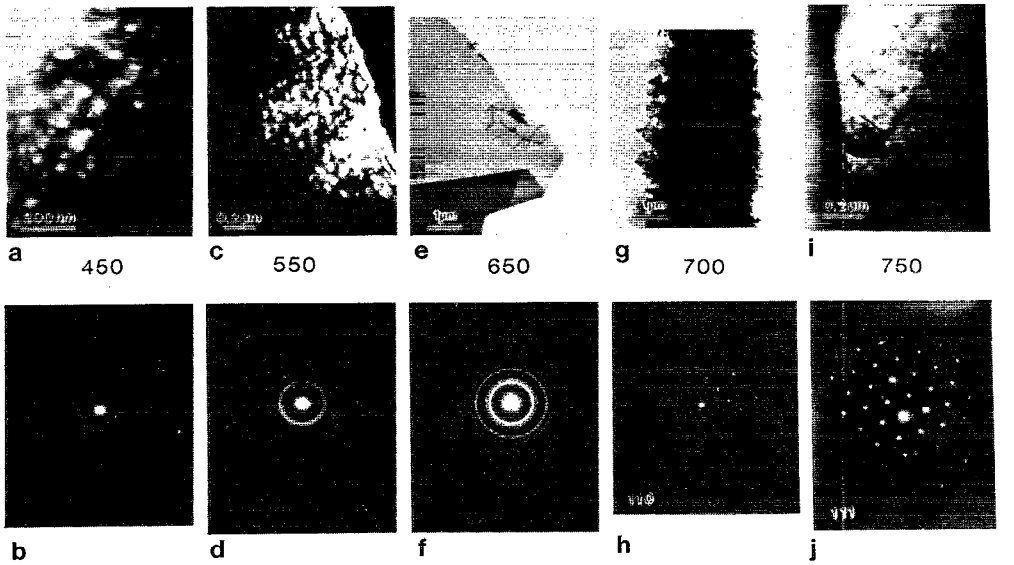

FIG. 3. The microstructural development of the PZT film as a function of annealing temperature.

skite phase, the strain was thermally relieved completely, and the bend contours disappeared, as can be seen in Fig. 3(i). In Fig. 2(b), in addition to the single [110] spot pattern from the perovskite phase, a faint pyrochlore ring [arrowed in Fig. 2(b)] was also observed. Since this diffraction pattern arose from the area which was completely within the perovskite particle, the only reason for the existence of the pyrochlore ring is that the perovskite particle is actually sitting on top of a much thinner pyrochlore film; in other words, the perovskite phase grows on top of the pyrochlore film.

Figure 3 is a set of TEM micrographs showing the development of the perovskite phase as a function of annealing temperatures. For an annealing temperature at or below 550 °C, the microstructure has a mottled structure and the corresponding electron diffraction shows a single-diffuse ring which indicates an amorphous structure. More careful examination of the diffuse ring reveals that the d spacing of the diffuse ring corresponds to the d spacing of the most intense (222) ring of the pyrochlore phase. Based on this information, we can assume that the pyrochlore phase has already nucleated and formed very minute clusters at temperatures as low as 450 °C. At 650 °C annealing, well-defined pyrochlore grains are formed and the corresponding sharp diffraction-ring pattern signifies a well-defined grain structure. In addition to the presence of the fine-grain pyrochlore phase, a few clusters of three to four perovskite grains are found and appear to grow out from the pyrochlore phase, as can be seen in Fig. 3(e). At a higher annealing temperature, more perovskite grains are formed and each grain can be identified by the characteristic diffraction spot pattern; see Fig. 3(f). At a 750 °C annealing, all of the pyrochlore phase has transformed to perovskite phase, as shown in Fig. 3(i). Nevertheless, the perovskite-transformation temperature is not unique for the free-standing PZT films, but found to be thickness dependent. Very thin PZT films in our study did not transform to perovskite phase even after 750 °C annealing. For instance, many samples with tapering film thicknesses had the perovskite phase formed at the thicker areas whereas the thinner regions remained in a pyrochlore structure.

From the theoretical calculations, the density of the perovskite phase is 8.05 g/cm^3 and that of the pyrochlore phase is 7.55 g/cm^3. Thus, a decrease in volume is expected to accompany the pyrochlore-perovskite transformation. For the free-standing films, especially for the very thin samples, the strain energy required to form the perovskite phase is diminished due to the strain relaxation in the direction normal to the film. Hence, the transformation temperature observed is always lower than the transformation temperature determined by the x-ray method. Nevertheless, the TEM study of the PZT thin films has demonstrated the pertinent evolution of the pyrochlore to perovskite transformation.

In conclusion, a new TEM sample-preparation method was suggested and used in this study. The microstructural changes of PZT films were studied by TEM. The pyrochlore phase is shown to have very fine-grain structure and the perovskite phase is observed to grow on the pyrochlore phase at a temperature around 650 °C. The discrepancy of the transformation temperature is discussed and can be attributed to the size effect of the thin films.

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